



TITLE:

# Studies on the Synthesis and Reactions of Ethyl $\alpha$ -Formyl Stearate

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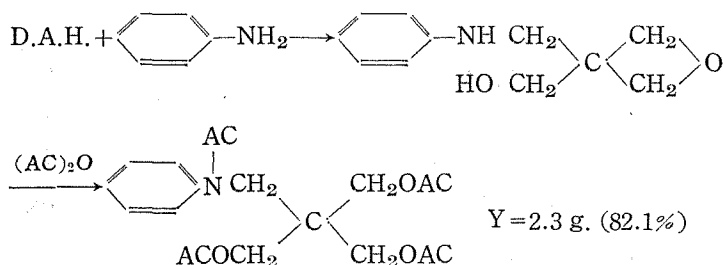
**Reaction of D.A.H. with aniline.** D.A.H. (0.74 g.) was heated with 4.1 g. aniline at 190~200°C for 12 hrs. and the excess aniline was removed by vacuum distillation. The obtained semi-solid product was acetylated with acetic anhydride and colourless crystal (m.p. 165.5-166°C) was obtained.

Analytical value of the acetylated product:

Calcd. for  $C_{19}H_{25}O_7N$  N, 3.69 ; Mol. Wt., 379

Found N, 3.56 ; Mol. wt., 351

From the above data it can be concluded that the reaction has proceeded in the way as follows:



The authors have also attempted the reactions of D.A.H with Grignard reagent, Na-ethylacetoacetate or higher alcohol, but no reaction can be recognized.

It is surprising that the D.A.H.-ring is very stable and unreactive compared with the analogous epoxy-ring compounds.

## 16. Studies on the Synthesis and Reactions of Ethyl $\alpha$ -Formyl Stearate

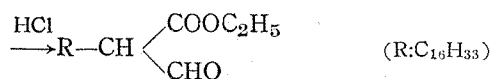
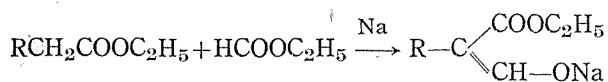
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$\alpha$ -Formyl-compound of fatty acid ester is generally produced by the reaction between fatty acid ester and ethyl formate using metallic sodium or sodium alcoholate as catalyst. Many examples of this  $\alpha$ -formylation reaction are well known about lower fatty acid esters, but not about the higher.

Therefore the authors have attempted this reaction with ethyl stearate and succeeded in the synthesis of ethyl  $\alpha$ -formylstearate and the authors have further tried some reactions of this  $\alpha$ -formylstearate with various passive components.

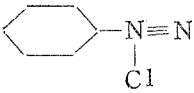
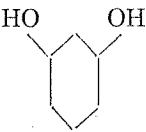
### I. Synthesis of ethyl $\alpha$ -formylstearate.



The mixture of 50 g. of ethyl stearate and 12 g. of ethyl formate was added in dry ether under ice-cooling in which 3.8 g. of metallic sodium was suspended and was stood for several days. The obtained Na-salt was dissolved in water, neutralized with HCl and extracted with ether. Twenty seven grams of ethyl  $\alpha$ -formyl stearate was obtained. Yield 49.6%, m.p. 64°C.

## II. Reactions of Ethyl $\alpha$ -Formylstearate.

Ethyl  $\alpha$ -formylstearate was reacted with various passive components, the results are summarized in the following:

Passive component	Product	Yield(%) m.p. (°C)	N% found (calcd.)
1. $\text{NH}_2\text{NH}_2$	$\begin{array}{c} \text{R}-\text{CH}-\text{CH} \\   \quad \quad \quad \parallel \\ \text{O}=\text{C} \quad \quad \text{N} \\ \quad \quad \quad \diagup \\ \quad \quad \quad \text{NH} \end{array}$	46.8 108	8.65 (9.02)
2. $\text{NH}_2\text{OH}$	$\begin{array}{c} \text{R}-\text{CH}-\text{COOC}_2\text{H}_5 \\   \\ \text{CH}=\text{NOH} \end{array}$	67.0 55	3.65 (3.94)
3. $\text{NH}_2\text{NHCONH}_2$	$\begin{array}{c} \text{R}-\text{CH}-\text{COOC}_2\text{H}_5 \\   \\ \text{CH}=\text{NNHCONH}_2 \end{array}$	35.9 73	10.10 (10.57)
4. $\text{NH}_2\text{CSNH}_2$	$\begin{array}{c} \text{NH}-\text{CH} \\ \diagup \quad \diagdown \\ \text{S}=\text{C} \quad \quad \text{C}-\text{R} \\ \diagdown \quad \diagup \\ \text{NH}-\text{CO} \end{array}$	42.5 97	7.37 (7.96)
5. 	$\begin{array}{c} \text{R}-\text{C}-\text{COOC}_2\text{H}_5 \\ \parallel \\ \text{NNH}-\text{C}_6\text{H}_{11} \end{array}$	30.7 56	6.33 (6.70)
6. 	$\begin{array}{c} \text{HO} \quad \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{C}-\text{R} \\ \quad \quad \quad \diagup \\ \quad \quad \quad \text{CH} \end{array}$	61.8 75	401 found } mol. 386 calcd. } wt.

## 17. Joint Reaction by Formaldehyde

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Formaldehyde is a distinguished active component and joints any two passive components ( $\text{P}_1\text{H}$  and  $\text{P}_2\text{H}$ ) in the manner as follows:

